Improvement of proton exchange membrane fuel cell performance in low-humidity conditions by adding hygroscopic agarose powder to the catalyst layer

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HIGHLIGHTS

- A self-humidifying MEA is prepared by adding agarose to the anode catalyst layer.
- The MEA shows excellent self-humidification performance at 60 °C and 20% RH.
- The current density is up to 500 mA cm^{-2} at 0.7 V at 60 °C and 20% RH condition.
- The long term testing of 10 h reveals the good stability of the MEA at low RH.

GRAPHICAL ABSTRACT
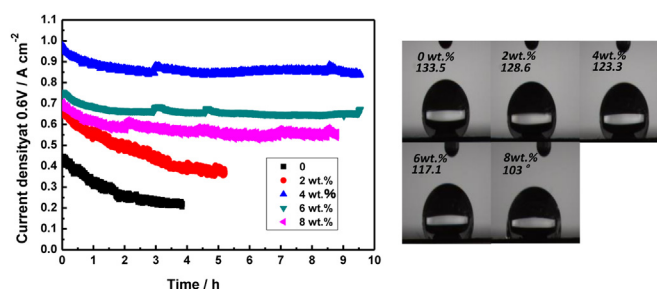
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ABSTRACT

A high-performance membrane electrode assembly (MEA) with agarose added to the anodic catalyst layer (CL) was successfully prepared. The MEA exhibited excellent performance at low relative humidity (RH) in an air/hydrogen proton exchange membrane fuel cell. The effects of agarose content, RH, cell temperature, and back pressure on the low-humidity performance of this MEA were investigated. The results of water contact angles and water uptake measurements reveal that the hydrophilicity of the anode is significantly improved with the addition of agarose. With a low RH of 20% and a cell temperature of 60 °C, the optimal MEA (MEA-4), containing 4 wt.% agarose in the anode CL, achieves excellent low-humidity performance: the current density reaches 960 mA cm^{-2} at 0.6 V and 500 mA cm^{-2} at 0.7 V. After 10 h of continuous operation under the same conditions, the current density decreases just slightly, from 960 to 840 mA cm^{-2}, whereas the current density of a blank MEA without added agarose degrades sharply.

1. Introduction

Developing a self-humidifying membrane electrode assembly (MEA) that would make it possible for a MEA or proton exchange membrane fuel cell (PEMFC) to operate in conditions of low or no humidity has recently become an attractive topic in the field of fuel cell research. A MEA with high-performance and self-humidifying could simplify fuel cell systems, decrease their cost, and make fuel cell water management easy—all factors that would accelerate the commercialization of PEMFCs.

A facile and effective method of preparing a self-humidifying MEA is to add hygroscopic materials into the anode catalyst layer (CL). Some researchers have reported [1–13] that the addition of hygroscopic SiO_2, Al_2O_3, PVA, or ZnO particles into the anode CL

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could improve the wettability of MEA and thus enhance its performance under low or no humidity conditions. Jung et al. [1] prepared a self-humidifying MEA by directly dispersing hydrophilic SiO_2 particles into the anode CL. The MEA's wettability and performance under low-humidity conditions were remarkably improved. With 0% relative humidity (RH) at the anode and 80% RH at the cathode, an MEA with 40 wt.% SiO_2 in the anode CL exhibited better performance than a blank MEA: the current density at 0.6 V reached 840 mA cm^{-2}, although they did not provide long-term discharge data. Inoue et al. [12] prepared CLs containing SiO_2 nanoparticles (SiO_2–CLs) to improve the low-humidity performance of a PEMFC. The cell achieved the highest performance when SiO_2–CLs were used for both the anode and the cathode; at 30% RH and 80 °C, the current density at 0.7 V was 2.7 times larger than that of without SiO_2. Su et al. [5] fabricated a Pt–SiO_2/C self-humidifying catalyst via an organic colloid method. When this catalyst was used in the anode CL, at a cell temperature of 50 °C and 28% RH for both anode and cathode, the current density at 0.6 V remained at 0.65 A cm^{-2} without any degradation for 20 h. It was suggested that the silica on the carbon support served as a mini water reservoir, absorbing back-diffused water from the cathode layer and thereby improving the low- or non-humidification performance of the PEMFC. Liang et al. [11] attempted to prepare a self-humidifying MEA by adding polyvinyl alcohol (PVA) —an organic polymer material rather than an inorganic one—to the anode CL; the operating temperature of this MEA was up to 50 °C at an RH of 34%, with the current density at 0.6 V reaching 1000 mA cm^{-2} and remaining at 750–780 mA cm^{-2} after 60 h of constant voltage testing.

Some researchers [14–20] prepared self-humidifying MEAs by inserting a hydrophilic layer between the gas diffusion layer (GDL) and the CL. The MEAs with a thin hydrophilic layer coated on the carbon paper effectively avoided membrane dehydration and cathode flooding, enabling them to achieve high performance in low humidity. Nonetheless, although great progress has been achieved, there is still a long way to go before a self-humidifying MEA is developed that meets the requirements for practical use and commercialization.

Agarose is a natural polysaccharide polymer material, generally extracted from seaweed, with a linear polymer made up of repeating units of agarobiose. Its water uptake is 98–99%, and it is highly stable—characteristics that make it a potential hygroscopic additive in self-humidifying MEA applications. As part of our continuing endeavors to prepare self-humidifying MEAs, in the present study we added agarose to the anode CL. As expected, the MEAs exhibited excellent self-humidifying performance under low humidity at a cell temperature of up to 60 °C.

2. Experimental

2.1. Preparation of MEAs

MEAs with an active area of 5 cm^2 were fabricated using a direct catalyst spraying technique developed in our laboratory [21]. Before spray deposition of the catalyst layers, Nafion 212 membranes (DuPont, USA) were pretreated using a standard procedure: treatment in a 5 wt.% H_2O_2 solution at 80 °C for 1 h, followed by treatment in deionized water at 80 °C for 1 h, then in 0.5 M H_2SO_4 solution at 80 °C for 1 h, and finally in deionized water again at 80 °C for 1 h. Anode catalyst inks were prepared by mixing commercial Johnson Matthey HiSPEC 4100 Pt/C catalyst (40 wt.%), agarose powder, isopropanol, and 5 wt.% Nafion solution (DuPont, USA). The cathode catalyst ink was prepared by the same method, but without agarose. The Pt loadings at the anode and cathode were 0.1 and 0.2 mg cm^{-2}, respectively, and the dry Nafion content in the

anode and cathode CLs was adjusted to 25 wt.%. The anode CL and cathode CL were prepared by spraying the catalyst ink onto both sides of the pretreated membrane. In this work, we prepared four MEAs, with anode CL agarose contents of 2, 4, 6, and 8 wt.%, which we refer to as MEA-2, MEA-4, MEA-6, and MEA-8, respectively. For comparison, we also prepared a MEA without adding agarose, which we call MEA-0.

2.2. Measurement of anode catalyst layer contact angle

The sessile drop method is the most common means of measuring the contact angle of a liquid on a solid surface. Using this technique, we set a drop of water on the surface of the anode CL and measured the contact angle by fitting a tangent to the three-phase point where the liquid surface touched the solid surface. To characterize the wetting property of the CL of our MEAs, we determined the contact angle of a water drop on the CL experimentally by direct image analysis of the shape of the drop at room temperature.

2.3. Measurement of water uptake

The water uptake of the anode CL was measured by a method described in the literature [11], whereby the wet weight was measured after immersing the sample in hot water for 4 h, and the dry weight was measured by drying the membrane at 80 °C for 4 h. The water uptake (%) was calculated using the following equation:

$$Wup\% = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\%$$

where m_{wet} and m_{dry} are the weights of the wet and dry samples (g), respectively.

2.4. Single-cell tests

A MEA was assembled using a catalyst-coated membrane and two pieces of GDL without hot pressing, and performance testing was carried out in a standard single cell with an active area of 5 cm^2, using a Fuel Cell Testing System (Arbin Instruments, USA). Pure hydrogen and compressed air were fed to the anode and cathode, respectively, at flow rates of 300 ml min^{-1} (hydrogen) and 800 ml min^{-1} (air). Before the performance test, the cells were activated in a continuous discharge mode until stable performance was obtained; the activation was processed at a cell temperature of 70 °C and with 100% humidification of the hydrogen and air. The cell performance at various RH levels was measured at a cell temperature of 60 °C, with the back pressures of both hydrogen and air at 30 psi. The temperatures of the gas lines to the anode and the cathode were always set at 5 °C above the humidification temperatures to prevent water condensation.

2.5. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) was used to study the polarization resistance of the MEAs, using a Zahner IM6e electrochemistry station (Zahner, Germany). These measurements were carried out at a cell potential of 0.8 V, with amplitude of 5 mV, and in the frequency range of 0.1 Hz–1 kHz.

3. Results and discussion

Fig. 1 presents photographs of the contact angles of the anode CLs with and without the addition of agarose. The water contact angles of the anode CLs with 0, 2, 4, 6, and 8 wt.% agarose were 133.5, 128.6, 123.3, 117.1, and 103°, respectively, showing that the
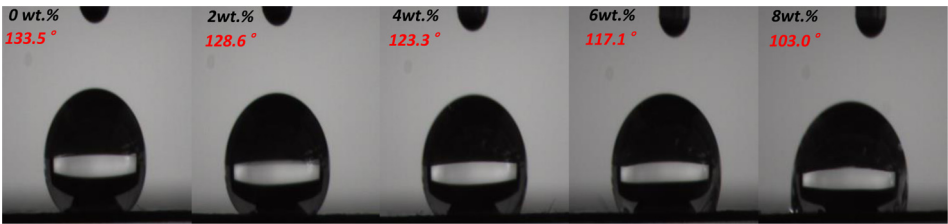
Fig. 1. The contact angles of MEAs with different amounts of agarose in the anode catalyst layer.

wettability of the anode CL was significantly improved by the addition of agarose and strongly related to the amount added: the greater the amount, the lower the contact angle.

To date, water management remains one of the key challenges for PEMFCs, since the ionic conductivity of the Nafion membrane and the Nafion ionomer in the CL is strongly dependent upon the amount of water available in the membrane and CL [22,23]. Fig. 2 shows the water uptake of anode CLs with different agarose contents. It can be seen that the water uptake rises from 43.2 to 168.8% as the amount of agarose increases from 0 to 8 wt.%. These results might be higher than the actual water absorption values because a CL with a microporous structure can absorb more water. Nevertheless, the measurement errors of all the CLs should be similar because the samples were prepared by the same method and measured using the same procedures. Hence, the results still show that the water uptake of the anode CL improves when it contains agarose. However, too much agarose in the CL may have an adverse effect on the MEA's ionic or electrical conductivity. As the result, the cell resistance would be increased, as we will discuss later (see Table 1), because agarose is an insulative material. Furthermore, it is impossible to establish a simple proportional relation between the water uptake and the MEA performance. So, the optimal amount of agarose in the anode CL has to be determined by single-cell tests.

Fig. 3(a) plots the performance of MEAs containing various amounts of agarose in the anode CL and their corresponding impedance spectra at 60 °C and 100% RH for both cathode and anode. It can be seen that the performance of MEA-2 and MEA-6 is almost the same as that of MEA-0, indicating that the addition of agarose has no negative effect on MEA performance with under full humidity; conversely, over the whole current density area, MEA-4 exhibits obviously superior performance to MEA-0, while MEA-8

exhibits inferior performance. These findings reveal that the introduction of an appropriate amount of agarose not only does not damage MEA performance, but actually improves it somewhat at full humidification; this may be attributable to the adsorption of water by agarose, which helps the back-diffusion of water molecules transfer from cathode to anode, then facilitates the release of water from the cathode and thereby prevents flooding.

Table 1
Ohmic resistance (R_Ω) and charge transfer resistance (R_{ct}) of single cells with various MEAs.

MEA	MEA-0	MEA-2	MEA-4	MEA-6	MEA-8
R_Ω (Ω cm^2)	1.018	0.673	0.567	0.632	0.790
R_{ct} (Ω cm^2)	0.424	0.472	0.346	0.419	0.466

Fig. 2. Water uptake of MEAs containing various amounts of agarose, measured at room temperature.
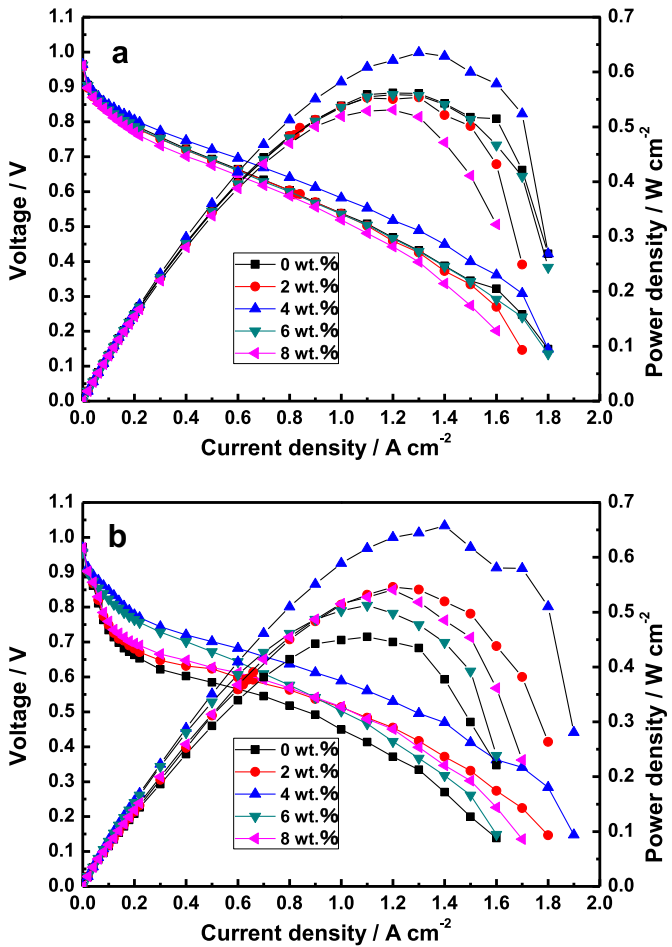
Fig. 3. Performance comparison of MEAs with different amounts of agarose. Single cells operated at 60 °C and 30 psi back pressure, under 100% RH (a) and 20% RH (b) for both anode and cathode.
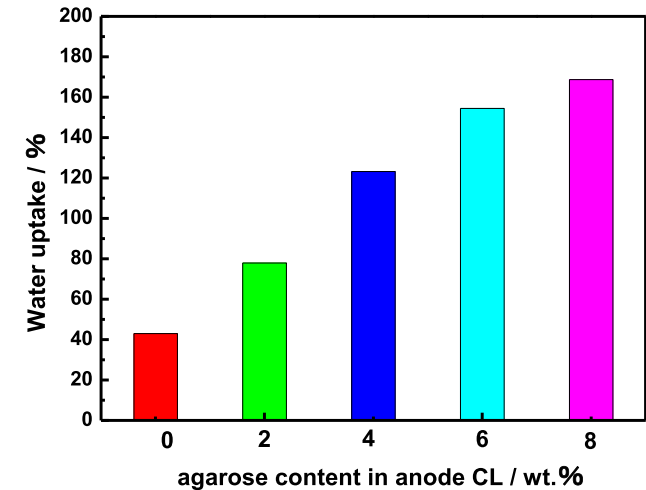
Under low-humidity conditions, increased ionic resistance in the cell may decrease its performance, especially at high temperatures [24]. The water at the anode is mainly supplied by the water that back-diffuses from the cathode due to the water concentration gradient. If the anode CL can increase the water back-diffused from cathode to anode, MEA performance may be enhanced under low humidity. As shown in Fig. 3(b), the low-humidity performance of the MEAs greatly improved with the addition of agarose, all of them showing better performance than the blank MEA over the whole investigated current density range at 60 °C and 20% RH. This was possibly because the agarose in the anode CL acted as a reservoir, retaining water and accelerating water transportation from cathode to anode, thus keeping the membrane and anode CL at a proper hydration level under low humidity.

The optimal amount of agarose in the anode CL was ca. 4 wt.%, yielding a current density of 500 mA cm^{-2} at 0.7 V, 3.5 times that of MEA-0 (140 mA cm^{-2}). With greater or lesser amounts of agarose, the performance decreased slightly. This explicitly indicates that introducing the appropriate amount of agarose into the anode CL can improve MEA performance under low-humidity conditions, but too much agarose (which can act as an insulator) may affect the transportation of electrons and protons, while too little will not improve the back-diffusion of water.

To obtain further information about how agarose in the anode CL affected cell performance, we measured the EIS of the MEAs at a cell voltage of 0.8 V, as shown in Fig. 4. From Fig. 4 and Table 1 we see that the cell's ohmic resistance (R_Ω) dropped significantly as the amount of agarose in the anode CL increased. This can be explained by the increase in water back-diffused from cathode to anode due to the hydrophilic agarose; having sufficient water in the anode layer and membrane facilitated proton transmission and reduced the ohmic resistance.

It is interesting that MEA-4 not only yields the lowest ohmic resistance, but also shows the lowest charge transfer resistance (R_{ct}) during the oxygen reduction reaction [25], in accordance with the cell performance discussed earlier. At this point, we have no explanation for this phenomenon.

Fig. 5 compares the effect of different RH levels on the performance of MEA-4. It is remarkable that the MEA exhibited almost the same performance when the RHs of both anode and cathode went from 100% to 62%. Once the RH was further decreased to 37% and 20%, the performance was just slightly reduced in the low
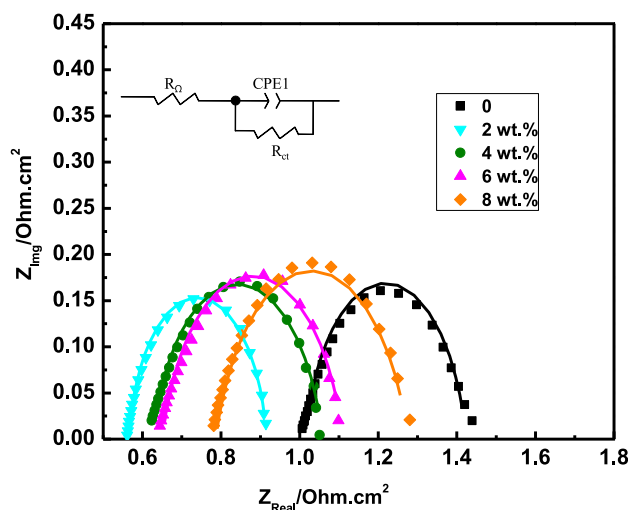
current density region, but returned to some extent at high current densities, revealing the excellent low-humidity performance of MEA-4.

Fig. 6(a) shows the effects of cell temperature on the performance of MEA-4 at a low RH of 20%. For clarity, we plotted the
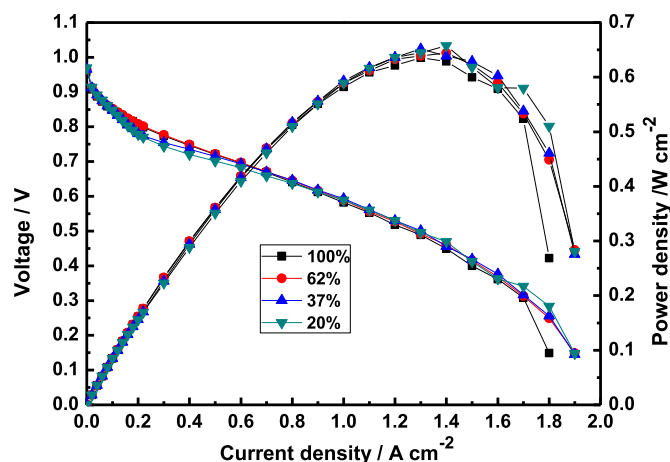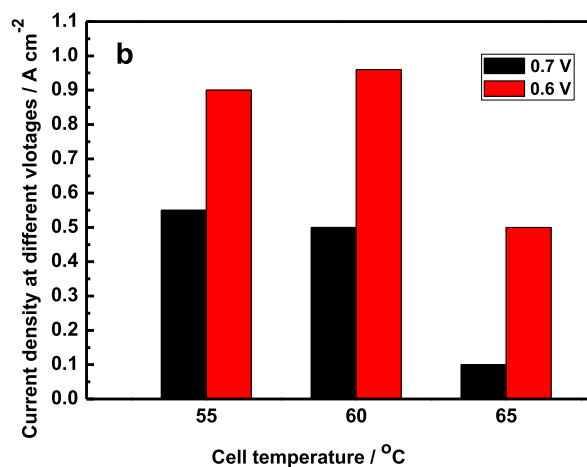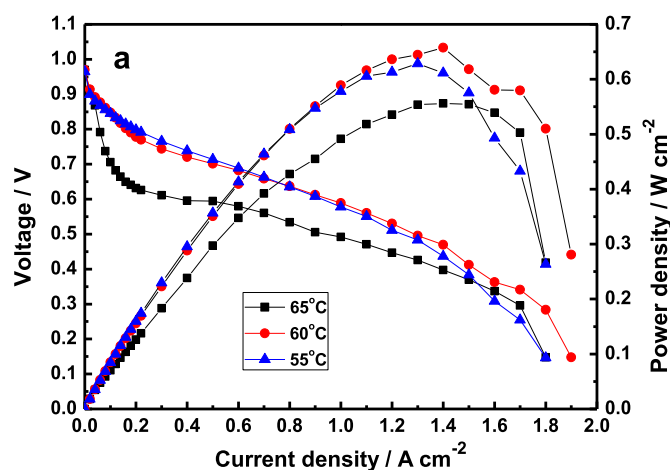
Fig. 5. The performance of MEA-4 under various RH conditions; the cell temperature is 60 °C and the back pressure is 30 psi for both anode and cathode.

Fig. 6. The performance of MEA-4 operated at different cell temperatures (a); current density versus cell temperature at 0.6 V and 0.7 V (b). 20% RH and 30 psi for both anode and cathode.

Fig. 4. The impedance spectra of MEAs containing various amounts of agarose, measured at 60 °C and 30 psi, 100% RH of anode and cathode.

current density at 0.6 V and 0.7 V with different cell temperatures, as shown in Fig. 6(b). We found that at 60 °C (around the real operating temperature of a PEMFC), the MEA performed somewhat better than at 55 °C; the current densities at 0.6 V were 960 mA cm^{-2} and 900 mA cm^{-2}, respectively. This slight superiority may be due to a kinetics factor, as a lower temperature leads to lower kinetics performance. At 65 °C, however, the performance decreased sharply, possibly because water generated at the cathode quickly evaporated, decreasing back-diffusion and thereby causing dehydration of the MEA, especially at low humidity. This result is in agreement with that reported by Vengatesan et al. [26]. The optimal cell temperature for our agarose added MEA seems to be 60 °C.

We also investigated the effects of back pressure on cell performance at 60 °C and 20% RH. As shown in Fig. 7, the performance significantly increased as the anode and cathode back pressure increased, which is understandable from a thermodynamics point of view. The increase in the back pressure produced more power, which had a favorable effect on cell performance. The same outcome has been observed in previous studies [21,27].

To investigate the self-humidification stability of the agarose-containing MEAs under low humidity, we conducted long-term continuous discharge testing for 10 h at 20% RH using MEA-0, MEA-2, MEA-4, MEA-6, and MEA-8 (Fig. 8). At 0.6 V, the current density of MEA-0 decreased rapidly throughout. In contrast, the performance and stability of the MEAs containing agarose in the anode CL were significantly enhanced. MEA-4, MEA-6, and MEA-8 exhibited excellent stability at low humidity, their performance fading by 10% within 2 h but then stabilizing. Although MEA-2 showed better performance and stability than MEA-0, its results were inferior to those of MEA-4, MEA-6, and MEA-8, indicating that more than 2 wt.% agarose is needed in the anode CL to achieve excellent low-humidity performance and stability. MEA-4 exhibited the best performance and stability: its current density at 0.6 V reached 960 mA cm^{-2} and remained stable at 840 mA cm^{-2} after 10 h of operation, making this MEA a potential candidate for practical applications.

What is the self-humidification mechanism when agarose is added? Fig. 9 presents a schematic diagram of agarose-promoted back-diffusion of water from cathode to anode. Due to its strong water adsorption, agarose in the anode CL acts as a water-drawing agent, a mini water reservoir, and a transportation chain of water molecules, promoting water retention in the anode CL, reinforcing water back-diffusion from cathode to anode, transporting water molecules to protons, and facilitating proton hydration and transfer, giving the MEA high performance and high stability at low humidity.
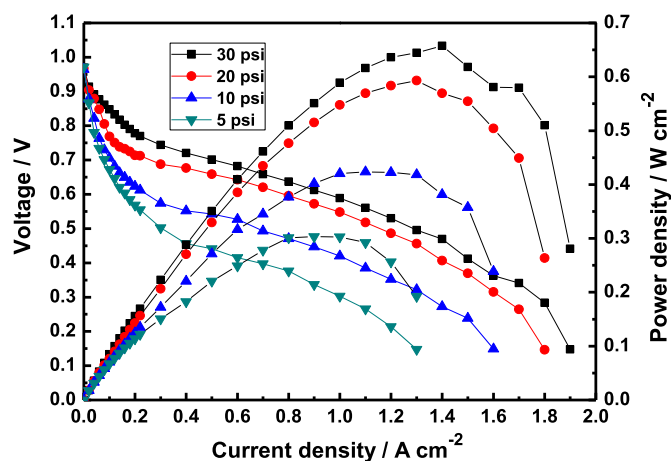

Fig. 7. The performance of MEA-4 at various back pressures. Cell temperature is 60 °C and RH is 20% for both anode and cathode.
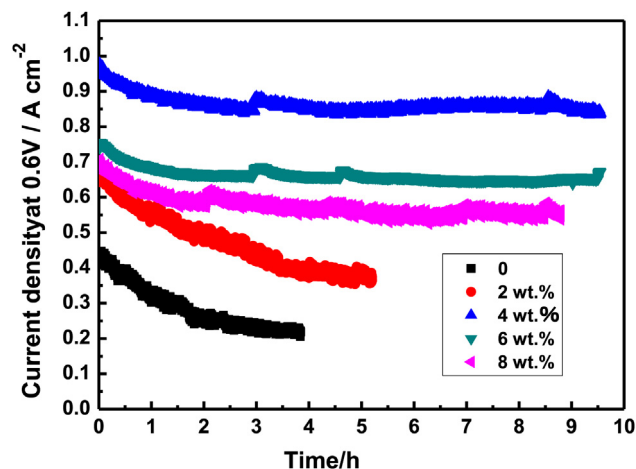

Fig. 8. Long-term discharge curves of MEAs operated at 60 °C, 30 psi back pressure, and 20% RH. The hydrogen and air flow rates were 300 and 800 ml min^{-1}, respectively.
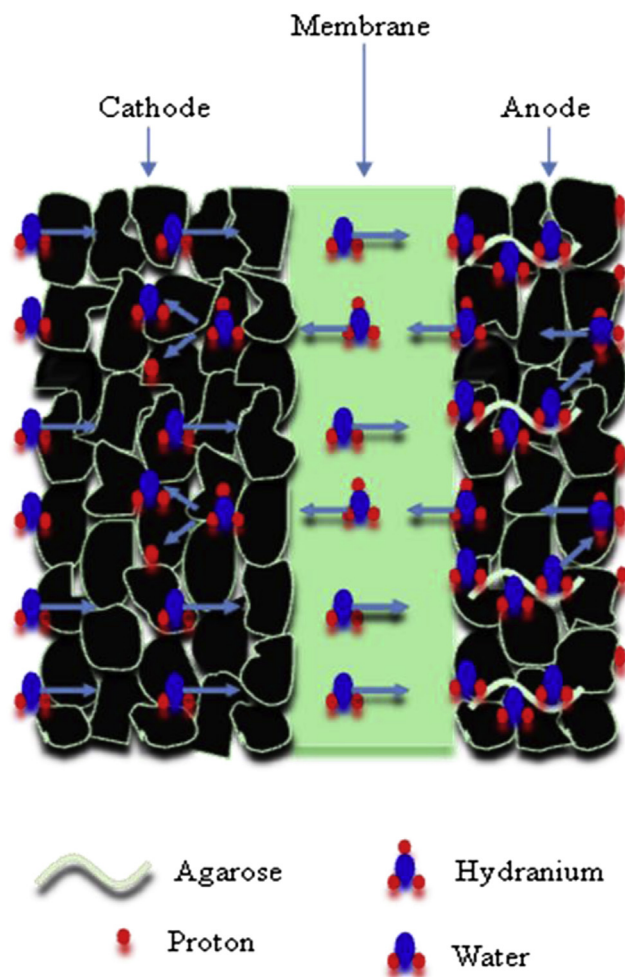

Fig. 9. A schematic diagram of a self-humidifying MEA with agarose (ME) in the anode CL.

4. Conclusions

Novel self-humidifying MEAs were successfully prepared by adding hydrophilic agarose into the anode CL; MEAs containing agarose achieved high performance and excellent stability at very low humidity. MEA-4, containing 4 wt.% agarose, yielded the best results: the current density at 0.6 V and 0.7 V reached 960 mA cm^{-2} and 500 mA cm^{-2}, respectively, and remained at 840 mA cm^{-2} after 10 h of long-term testing at 20% RH and 60 °C. It was found that the addition of agarose resulted in lower ohmic resistance and lower charge transfer resistance. We suggest that the excellent low-humidity performance and stability of the MEAs containing agarose in the anode CL can be attributed to the high water adsorbing capacity of agarose; it may act as a water-drawing agent, a mini water reservoir, and a transportation chain of water molecules, facilitating the hydration of protons generated at the anode and their movement to the cathode under low-humidity conditions.

Acknowledgments

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